# INFLUENCE OF CARBONATION ON THE CHLORIDE ION DIFFUSION COEFFICIENT IN FLY ASH CONCRETE

**RAPHAELE MALHEIRO[*], GUSTAVO CAMACHO[*], AIRES CAMÕES[*], GIBSON MEIRA[†], TERESA AMORIM[*], RUI M. FERREIRA[††] AND RUI REIS[*]**

[*] Centre for Territory, Environment and Construction (CTAC)
University of Minho
Campus Azurém, Guimarães, Portugal
e-mail: raphamalheiro@gmail.com; gustavo92@live.com.pt; aires@civil.uminho.pt; mtamorim@det.uminho.pt; ruicunhareis@gmail.com, web page: http://www.ctac.uminho.pt

[†] Federal Institute of Education, Science and Technology of Paraíba (IFPB)
João Pessoa, Brazil
e-mail: gibsonmeira@yahoo.com, web page: http://www.ifpb.edu.br

[††] Technical Research Centre of Finland (VTT)
Espoo, Finland
e-mail: miguel.ferreira@vtt.fi, web page: http://www.vtt.fi

**Key words:** Chloride, Carbonation, Concrete, Fly Ash, Durability

**Abstract.** The incorporation of fly ash (FA) in cementitious matrices has been frequently used in order to make the matrix more resistant to the action of chlorides. On the other hand, it is known that $Ca(OH)_2$ existing in the matrix is consumed by the pozzolanic reactions, which makes easier the carbonation front advance. Given that the chloride ingress and carbonation are the two main causes of degradation in reinforced concrete, we speculate about the behaviour of FA concrete when the structure is submitted simultaneously to chlorides and carbonation.

This work studied the influence of carbonation on the chloride migration coefficient in FA concrete. For this, specimens with 0% and 40% replacement of cement CEM I 42.5R by FA were casted with water/binder 0.55 and 0.50 respectively. After 90 days of curing period, half of samples were subjected to accelerated carbonation (20ºC ,55%RH and 4%$CO_2$) for 1, 2 and 3 months. The other half was protected with plastic film during the same period. Non-steady-state migration tests, according to LNEC E463 (Portuguese specification), were performed with specimens subjected to both experimental conditions.

The results show that, for these conditions, the carbonation has a direct influence on chloride diffusion coefficient, increasing it. For FA concrete samples this effect is more evident. In these cases, the carbonated samples studied showed a diffusion coefficient up to two times higher than noncarbonated ones.

The increase in large capillary pores, caused by carbonation, can be responsible for the increase of chloride penetration into concrete subjected to combined action.

## 1 INTRODUCTION

To ensure the sustainability of the construction industry it is essential to guarantee the long term durability of concrete structures without unforeseen needs of maintenance. However, the premature deterioration of concrete structures has been observed worldwide, resulting in great financial losses, in the order of millions of euros [1] for repair and reconstruction of these structures, not including incalculable environmental and social impact. One option to address the sustainability and durability of concrete structures from the design phase has been to incorporate industrial wastes or byproducts into the mix as a partial replacement of cement.

In light of recent research internationally [2, 3, 4] more attention is now being drawn to the combination of degradation mechanisms and the effect on the concrete durability . Despite the advances in knowledge on concrete durability, little is known on how carbonation affects and interacts with chloride penetration.

The incorporation of fly ash (FA) in cementitious matrices has been used to make concrete more sustainable and also to make its matrix more resistant to the action of chlorides, as confirmed by published research [5, 6, 7]. However, taking into account carbonation, when replacing cement by FA there is a double effect: the reduction in matrix permeability, which reduces the penetration of carbon dioxide in the structure; the consumption of calcium hydroxide due to the pozzolanic reactions, which decreases the alkalinity of the concrete, resulting in a more rapid carbonation when compared to the concrete without pozzonalic addition [8, 9, 10].

The action of chloride ions and carbon dioxide on the concrete structures has been investigated as individual phenomena. However, the study on the combination of degradation mechanisms is relatively recent and achieves greater expressiveness from the year 2000 [11, 12, 13, 14, 15]. Thus, despite the combined action of these mechanisms being a reality, there is no consensus on the effect of combination of chlorides and carbonation on the durability of concrete with and without FA.

According to [11], for instance, for Ordinary Portland Cement (OPC) mortar, the exposure to carbon dioxide environment does not lower the chloride penetration resistance. They submitted the specimens to carbonation chamber (5% $CO_2$, 23ºC and 50% RH) for 28 days and after that, the specimens were tested for rapid chloride penetration test, modified rapid migration test and chloride immersion test (3% NaCl solution). On the other hand, [13] say that, for OPC concrete, after carbonation, the chloride diffusion coefficient increases. They submitted the specimens to carbonation chamber (20% $CO_2$, 20ºC and 70% RH) for 0,14 and 28 days. After that wet and dry cycle test was carried out. The specimens were immersion, for one week, in 5% NaCl solution and drying, for one week, in laboratory environment cycles to study the effect of carbonation on chloride transport. The cycles were repeated for twelve weeks.

In order to contribute to this important and ongoing scientific discussion, the main objective of this research is to study the effect of carbonation dioxide on chloride ion diffusion coefficient of concretes with incorporation of fly ash.

## 2 EXPERIMENTAL WORK

### 2.1 Materials and mixing proportion

In this work one has used Ordinary Portland Cement (OPC), CEM I 42.5R, and Fly Ash (FA) as binder materials, which chemical compositions are presented in Table 1. Fine aggregate with a fineness modulus of 5.04 and coarse aggregate with maximum size 12.70 mm were used. Tape water was used for all the produced mixtures.

**Table 1**: Chemical composition of OPC (CEM I 42.5) and FA

| Composition | OPC | FA |
|---|---|---|
| | % | % |
| $SiO_2$ | 20.33 | 55.10 |
| $Al_2O_3$ | 4.59 | 26.60 |
| $Fe_2O_3$ | 3.06 | 5.70 |
| CaO | 62.30 | 2.58 |
| MgO | 2.12 | 1.30 |
| $SO_3$ | 3.10 | - |
| $K_2O$ | 0.76 | 1.41 |
| $Na_2O$ | 0.19 | 0.26 |
| $TiO_2$ | - | 1.33 |
| $P_2O_5$ | - | 0.73 |
| $Cl^-$ | 0.07 | - |
| Loss on ignition | 1.78 | 3.07 |
| Insoluble residue | 1.21 | - |
| Remaining elements | 0.49 | 1.92 |

Two mixtures were adopted in this study, which are presented in Table 2. Cylindrical concrete specimens with ϕ100x200 mm were casted with the mixtures presented. After casting, the specimens were covered with a plastic sheet and were stored in a humidity chamber (21 ºC and 98% RH) for one day. Then, they were removed from the moulds and were cured immersed in water for 90 days. The choice of this curing period was to give enough time for pozzolanic reactions in specimens containing FA to occur.

**Table 2**: Mixtures and properties of thedeveloped concrete

| Materials | Binder | |
|---|---|---|
| | 100% OPC | 40% FA |
| *Relative proportions* | | |
| Cement (kg) | 380 | 228 |
| Fly ash (kg) | - | 152 |
| Water (l) | 209 | 190 |
| Sand 0/4 (kg) | 911.16 | 926.18 |
| Coarse aggregate 4/8 (kg) | 254.37 | 281.18 |
| Coarse aggregate 6/12 (kg) | 461.84 | 483.10 |
| *Property* | | |
| Slump (mm) | 100.5 | 110 |
| Compressive strength (MPa): | | |
| 28 days | 33.66 | 24.62 |
| 90 days | 45.16 | 34.48 |
| 365 days | 47.44 | 51.59 |
| Capillary absorption ($kg/m^2/min^{1/2}$) | 0.128 | 0.116 |
| Total porosity (%) | 10.5 | 9.99 |

## 2.2 Experimental program

After the curing period, all samples were cut in three slices. The top and bottom of the samples were discarded (Figure 1). The new samples (ϕ100x50mm) were divided in two groups, A and B. The group A was subjected to accelerated carbonation in carbonation chamber (4% $CO_2$, 20 ºC and 55% RH), following the recommendations of the European Standard [16], for 1, 2 and 3 months while the group B (reference group) remained in laboratory environment for the same period.

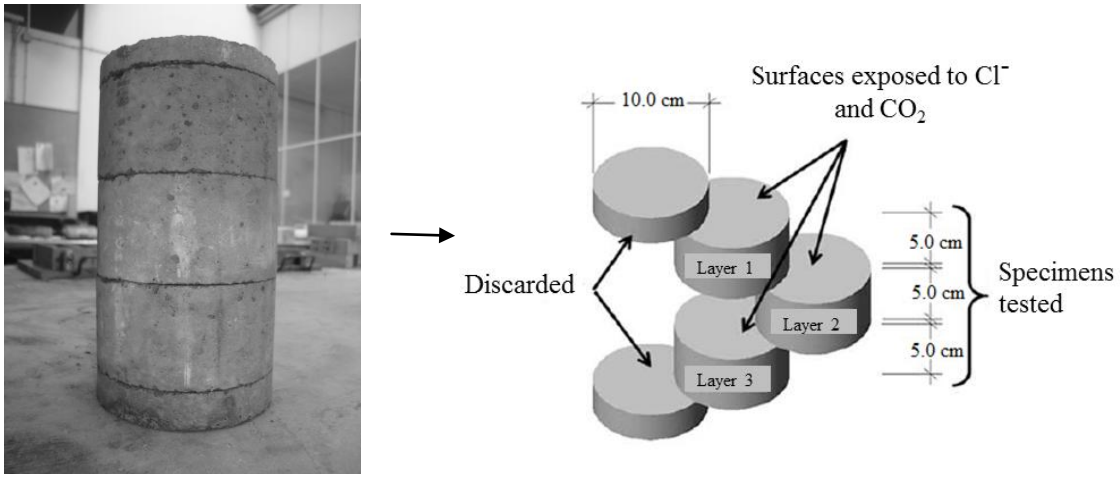


**Figure 1**: Scheme of sample utilization

Before accelerated carbonation the specimens of group A were subjected to preconditioning procedures in order to achieve the equilibrium with environmental humidity near 60% and accelerated the carbonation process. This preconditioning had three stages. In the first stage, the specimens remained in a chamber with controlled temperature and humidity (20 ºC and 60% RH) until to reach constant mass. Second, they had the lateral and the bottom covered with paraffin in order to guarantee the one-dimensional attack of aggressive agents through the top of the specimen. Third, they were protected with several layers of plastic film and put in an oven (40 ºC), for 20 days, to distribute the humidity inside the specimen. The specimens of group B were wrapped with plastic film and, after, they were stored in laboratory environment.

When finished the carbonation tests, Non-Steady-State Migration Tests (NMT) were performed [17] with specimens previously subjected to accelerated carbonation, group A, and with reference specimens, group B. For specimens of group A, the paraffin was removed and then all the specimens were subjected to NMT. These specimens were previously saturated with limewater under vacuum conditions and stored in the solution for 18 ± 2 h. Afterwards, the samples were placed in rubber sleeves, as it is shown in Figure 2. The catholyte was filled with a 10% NaCl solution and the anolyte with a 0.3M NaOH solution. The test duration and applied voltages were determined based on the initial current measured at 30 V.

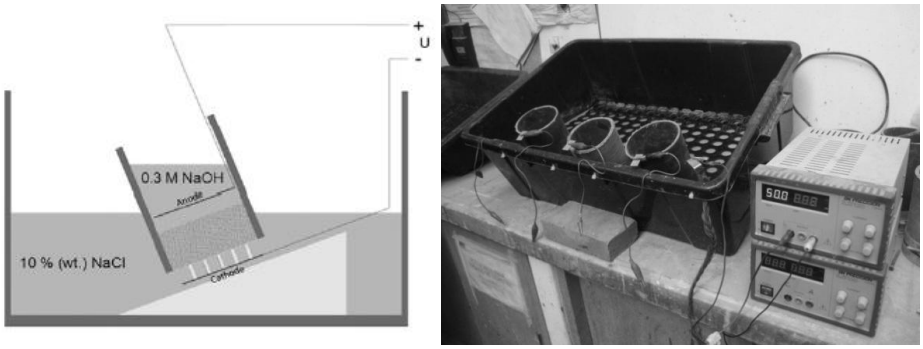


**Figure 2**: Non-Steady-State Migration Test scheme (a) and set-up (b)

At the end of the test, the samples were split perpendicularly to the aggressive agents penetration direction. For group B, the halfs were only sprayed with 0.1 M $AgNO_3$ solution in order to determine the penetration depth of chlorides. For group A, the halfs were used in different ways: the first one was sprayed with a 1% phenolphthalein solution in 70% ethyl alcohol [18] in order to determine the advance of the carbonation front; and the other one was sprayed with 0.1 M $AgNO_3$.

The penetration depth of chloride was used to determine a chloride ion diffusion coefficient and following equation derived from the Nernst–Plank equation [19] (1) where $D$ is chloride ion diffusion coefficient ($cm^2/s$), $R$ is gas content (8.314 J/K mol), $T$ is temperature (K), $L$ is the thickness of specimens (cm), $z$ is the ion valence, $F$ is Faraday content (9.65 x $10^4$ C/mol), $E$ is values of potential (V), $x_f$ is the inflection point of the chloride ion profiles that needs to be related to the depth given by the colorimetric technique and $t$ is the time of test duration (s).

$$D = \frac{RTL}{zFE} \times \frac{x_f}{t} \tag{1}$$

The schematic diagram of experimental program is shown in Figure 3.

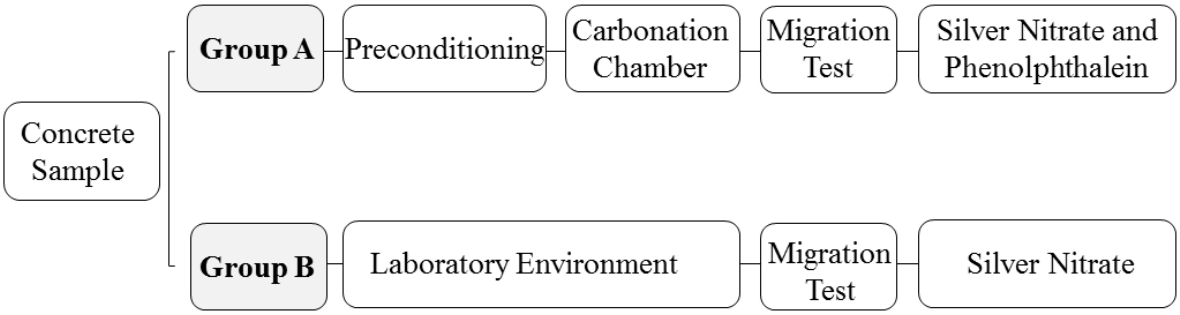


**Figure 3**: Schematic diagram of programs test

## 3 RESULTS

The next sections present results of concrete carbonation and chloride penetration. Each point represents an average of three specimens results.

### 3.1 Carbonation

Figure 4 shows the depth of carbonation front obtained for the specimens and exposure periods studied in group A. It is possible to see the results for OPC and FA concrete.

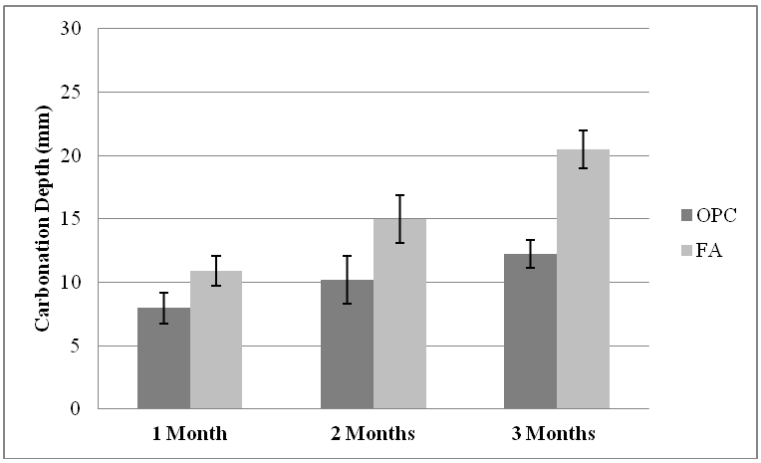


**Figure 4**: Carbonation depth for OPC and FA concrete in diferent test time

As expected, FA concrete presented deeper carbonation depth than OPC concrete. The difference between OPC and FA carbonation depth increases with the increase in testing time. In the third month this difference achieves 40.2%.

It can also be seen that there is an increase in carbonation depth with the increase of testing time. This increase is more pronounced in FA concrete where it is possible to see a 88% increase from first to third month.

### 3.2 Chlorides

Figures 5 and 6 show the chloride ion diffusion coefficients obtained from NMT, for OPC and FA concrete. Figure 5 shows the results for group B, reference group, only chlorides, and Figure 6 presents results for group A, carbonation and chlorides.

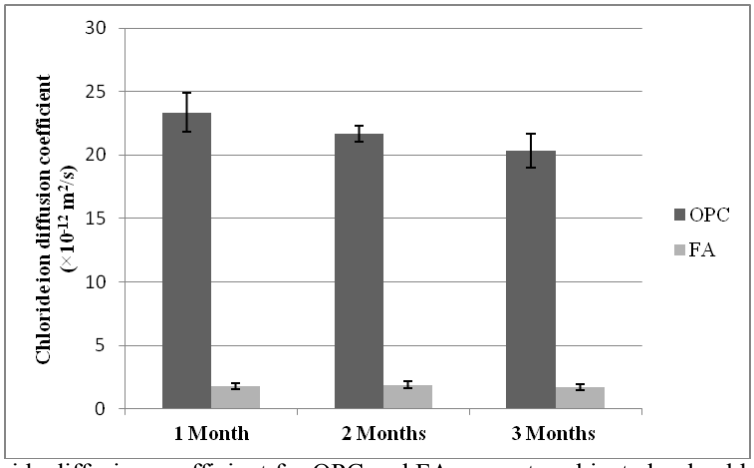


**Figure 5**: Chloride diffusion coefficient for OPC and FA concrete subjected only chloride action

As expected, OPC concrete has higher chloride ion diffusion coefficients than FA concrete. In the first month, the OPC diffusion coefficient, $23.35\times10^{-12}$ m²/s, is almost 13 times higher than FA diffusion coefficient, 1.90 $x10^{-12}$m²/s. In OPC concretes there is a tendency to decrease de diffusion coefficient with the test time increase. This tendency can be related with the development of cement hydration along time that decreases the concrete poros and, consequently, decreases the chloride diffusion coefficient. In FA concrete this tendency could not be observed.

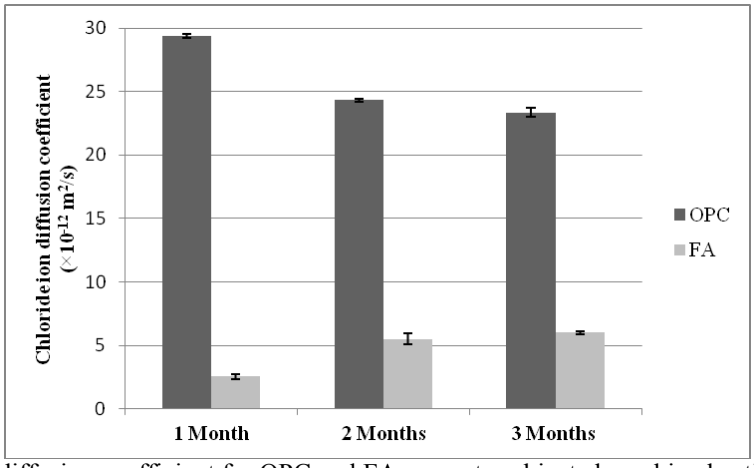


**Figure 6**: Chloride diffusion coefficient for OPC and FA concrete subjected combined action, $CO_2$ and $Cl^-$

In Figure 6 it is possible to observe the influence of carbonation on the chloride ion diffusion coefficient. Again, the OPC concrete presented higher chloride ion diffusion coefficients than FA concrete but, in this case, the diffusion coefficient values are higher than in the situation without carbonation, regardless FA presence. Thus, the results suggest that carbonation increases the chloride ion diffusion coefficient.

In OPC concretes there is a tendency to decrease the diffusion coefficient with the test time increase. But in FA concretes there is the opposite tendency, that is, the diffusion coefficient increase with the test time increase.

## 4 INFLUENCE OF CARBONATION ON CHLORIDE DIFFUSION COEFFICIENT

The results presented in section 3 show that the carbonation has influence on chloride ion diffusion coefficient of studied concretes.

For OPC concrete, under the studied conditions, there is an increase in diffusion coefficient when the samples are subjected to combined action of carbonation and chloride transport. In this case, the increase is more pronounced in the first month of carbonation where 7.96 mm of carbonation depth leads to a increase of 26% in chloride coefficient diffusion.

In the same way, for FA concretes (and deeper carbonation depths), under the conditions studied, the combined action increases the chloride diffusion coefficient. But, for this case, the coefficient of diffusion has increased (Figure 7). In the first month the increase is 44%, in the second month it is 191% and the third month has the biggest increase, 249%.

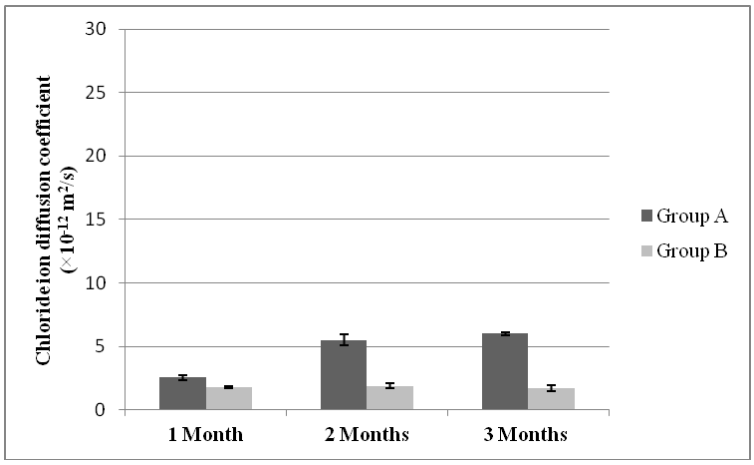


**Figure 7**: Chloride diffusion coefficient for FA concrete, group A and group B

Figure 8 shows the relationship between the chloride diffusion coefficient with carbonation depth in FA concrete.

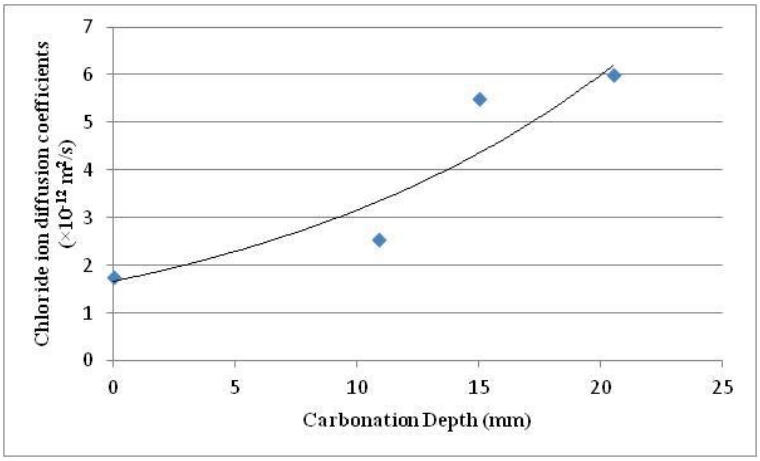


**Figure 8**: Relation between chloride diffusion coefficient and carbonation depth for FA concrete

This increase in chloride diffusion coefficient can be related with the increase in large capillary pores, caused by carbonation, providing a "privileged way" for chlorides. [20, 21] studied the effect of carbonation on pore structure and found that, after carbonation, there is a reduction in total porosity but the proportion of large capillary pores was increased slightly for the OPC pastes and much more significantly for FA pastes. Furthermore, the carbonated concrete has its chloride binding capacity reduced which means that there are more free chlorides.

Despite the large increase in the diffusion coefficient occurred in the FA concrete, it is important to say that the use of this material continues to be benefical in environments containing chlorides because it presents diffusion coefficients quite lower than OPC concrete, Figure 6. However, the use of FA in environments containing chlorides and $CO_2$, at the same time, should be considered with care.

Based on present results, it can be pointed out that carbonated concrete works as a "privileged way" for chlorides penetration. It is quite evident for FA concrete as we can see in Figure 9, that shows the FA concrete halfs (group A) after finished the test. It is possible to see that chlorides crossed completely the carbonated front but reached depths only a few millimeters deeper than the carbonation front.

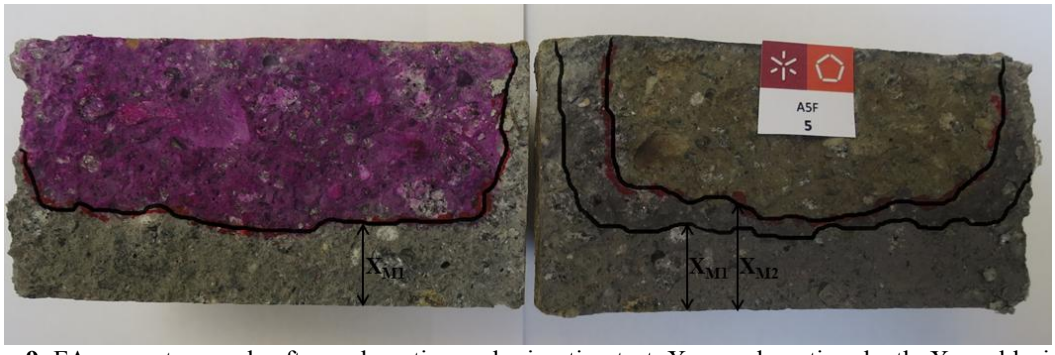


**Figure 9**: FA concrete sample after carbonation and migration test. $X_{M1}$: carbonation depth. $X_{M2}$: chloride penetration depth

## 5 CONCLUSIONS

Based on the results achieved it is possible to conclude, for the studied conditions, that:

- Carbonation has an influence on the chloride ion diffusion coefficient for OPC and FA concrete. Carbonated concrete works as a "privileged way" for chlorides penetration;
- For OPC concrete the carbonation increases the chloride diffusion coefficient up to 26%;
- For FA concrete the carbonation sharply increases the chloride diffusion coefficient. This increase achieves 249% for three months in carbonation chamber. Furthermore, the diffusion coefficient increases with the carbonation depth increase.

## REFERENCES

[1] DURAR – Durabilidad de la armadura. *Durability of reinforcement. Manual for inspection, evaluation and diagnostic of corrosión in reinforced concrete strcutures.* CYTED – Programa Iberamericano de Cinência y Tecnologia para el Desarrollo, (1998), pp. 208.

[2] Jung, S.; Choi, Y. and Lee B. *Influence of carbonation on the chloride diffusion in concrete*. In: Proceedings of the International Conference on Sustainable Building Asia, Seoul, (2007).

[3] Ramezanianpour, A., Ghahari, S. and Esmaeili, M. Effect of combined carbonation and chloride ion ingress by an accelerated test method on microscopic and mechanical properties of concrete. *Construction and Building Materials* (2014) **58**:138-146.

[4] Backus, J.; McPolin, D.; Holmes, N. and Long, A., *Combined chloride and carbon dioxide ingression in concrete exposed to cyclic wetting and drying*. Civil Engineering Research Association of Ireland. CERAI. Belfast, (28-29.08.2014).

[5] Chindaprasirt, P., Chotithanorm, C., Cao, H.T and Sirivivatnanon, V. Influence of fly ash fineness on the chloride penetration of concrete. *Construction and Building Materials* (2007) **21**:353-361.

[6] Cheewaket, T., Jaturapitakkul, C. and Chalee, W. Long term performance of chloride binding capacity in fly ash concrete in a marine environment. *Construction and Building Materials* (2010) **24**:1352-1357.

[7] Varga, I., Spragg, R., Bella, C., Castro, J., Bentz D. and Jason Weiss. Fluid transport in high volume fly ash mixtures with and without internal curing. *Cement and Concrete Composites* (2014) **45**:102-110.

[8] Neville, A. M. *Propriedades of concrete*. 2nd Edition., Pini, São Paulo, (1997).

[9] Vaghetti, A. O. *Effects of fly ash with rise husk ash or activated silica on carbonation of Portland cement concrete*. Master Thesis, Universidade Federal de Santa Maria, Santa Maria (1999).

[10] Sperb, J.E.K. *Carbonation and capillary absorption in concrete with mineral additions and chemical activatores*. Master Thesis, Universidade Federal de Santa Maria, Santa Maria (2003).

[11] Chindaprasirt, P., Rukzon, S. and Sirivivatnanon, V. Effect of carbon dioxide on chloride penetration and chloride ion diffusion coefficient of blended Portland cement mortar. *Construction and Building Materials* (2008) **22**:1701-1707.

[12] Kuosa, H., Leivo, M., Holt, E., Ferreira, R.M. *The effect of slag and fly ash on interaction of chloride penetration and carbonation*. Nordic Workshop on Durability aspects of fly ash and slag in concrete. Nordic Concrete. Oslo, (15-16.02.2012), pp. 57-66.

[13] Chengfang, Y., Ditao, N. and Daming, L. Effect of carbonation on chloride diffusion in fly ash concrete. *Disaster Advances* (2012) **5 [4]**:433-436.

[14] Malheiro, R.; Camões, A.; Ferreira, R.M.; Meira, G.; Amorim, T. *Effect of carbonation on the chloride diffusion of mortar specimens exposed to cyclic wetting and drying*. XIII International Conference on Durability of Building, Materials and Components, São Paulo, Brazil, (2014), pp.482-489.

[15] Malheiro, R., Camões, A., Ferreira, R.M., Meira, G., Amorim, T. and Reis, R. Carbonation front progress in mortars containing fly ash considering the presence of chloride ions. *Key Engineering Materials* (2015) **Sustainable Construction Materials**: 214-221.

[16] CEN/TS 12390-12. EUROPEAN COMMITTEE FOR STANDARDIZATION. *Testing hardened concrete - Part 12: Determination of the potential carbonation resistance of concrete: Accelerated carbonation method*, Brussels, (2010).

[17] LNEC E 463. Laboratório Nacional de Engenharia Civil. Betões. *Concrete. Determination of diffusion coefficient of chlorides from non-steady-state migration test*. Lisboa, (2004).

[18] RILEM CPC-18. REUNION INTERNATIONALE DE LABORATOIRES D´ESSAIS ET MATERIAUX. *Measurement of hardened concrete carbonation depth*. Materials and Structures (1988).

[19] Tang, L. and Nilsson, L. O. Rapid determination of the chloride diffusivity in concrete by applying an electrical field. *ACI Materials Journal* (1991) **89**:49-53.

[20] Ngala, V. T. and Page, C. L. Effect of carbonation on pore strucure and diffusional properties of hydrated cement pastes. *Cement and Concrete Research* (1997) **27**: 995-1007.

[21] Morandeau, A., Thiéry, M., Dangla, P. Impact of accelerated carbonation on OPC cement paste blended with fly ash. *Cement and Concrete Research* (2015) **67**: 226-236.

madrid 16

# Second International Conference on Concrete Sustainability

**13-15 June 2016**

# EBOOK

*Universidad Politécnica de Madrid / Technical University Madrid*

POLITÉCNICA
"Engineering the future"

INTERNATIONAL CAMPUS OF EXCELLENCE